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TIN CANS AND REFUSE INCINERATION: UPGRADING THE SCRAP*

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Abstract — In the series of investigations whether and how it is possible to reclaim the iron and tin constituents after incineration, several experiments were performed with the refuse incinerator of Amsterdam. The operating conditions were varied and the influence on the behaviour of the tin cans were determined. The degree of contamination and oxidation was established, just as tin losses and average tin content after incineration. Experiments with pyrolysis of scrap polyvinyl chloride in the presence of the incinerated tinplate showed that, from the earlier formed iron – tin alloy it is possible to reclaim almost all the tin, reducing the tin content in the cans to less than 0.05%, with iron losses not exceeding 5%.

INTRODUCTION

About 40% of Dutch domestic refuse is incinerated. Annual arisings contain approximately 40 000 t of tin cans.

In order to investigate whether it is possible to reclaim the iron and especially the tin constituents after incineration, the rates of diffusion and oxidation were determined of the iron – tin system over a range of temperature[1]. It appears that the thin layers of tin on the cans are converted very rapidly into iron – tin compounds, so that after incineration no free tins exists.

At temperatures of up to about 800°C, the tin from the iron – tin compounds diffuses at a rather slow rate into the iron base.

Oxidation of the iron – tin compounds of tin-plate with an initial tin-coating thickness of 1.2 μm in the presence of an excess of air occurs in 1¾ and 5 h at temperatures of 780 and 600°C, respectively. The oxidized layers can easily be removed from the iron base.

In addition to the above investigations, several experiments were performed with the refuse incinerator in Amsterdam.

Four series of cans of known composition were sent with the flow of refuse through the incinerator. On four successive days, the operating conditions were varied and the influence on the behaviour of the tin cans was determined. The average residence time of the cans on the furnace grate was about 1¾ h. During this time, some 35 – 50% of the iron was oxidized.

The separated cans were very dirty after incineration: approximately 35 – 55% of the dry weight consists of oxides and ashes. These oxides and ashes were carefully removed from the cans by hand. Compared with an original tin content of about 0.5%, the average tin content of the cleaned series varied between 0.3 and 0.4%, after incineration, representing about 40 and 30% respectively of the original tin.

The original tin in the seams was still present after incineration, representing about 8% of the original tin.

Concurrently, a series of pyrolytic experiments was carried out with different combinations of electroplated materials in an atmosphere of gaseous HCl. The HCl was produced by pyrolyzing scrap polyvinyl chloride[2]. These experiments showed that from the iron – tin alloy, as pre-

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sent in tin-plate leaving refuse incinerators, it is possible to reclaim almost all the tin, reducing the tin content in the body of the cans to less than 0.05% and with iron losses not exceeding 5%. Even the tin present in the seams can be reduced to less than 0.05% in this way.

EXPERIMENTAL

Short description of the refuse incinerator

The experiments were performed with the refuse incinerator of the city of Amsterdam. This plant consisted of 4 incinerating/steam generating units, each having an incineration capacity of 16 – 20 t of garbage per hour. Each unit was fitted with a sloping grate of 3 parallel sections with reciprocating bars according to a Martin Patent. Each grate section was equipped with a clinker discharge roll at the end. The primary combustion air was admitted through undergrate compartments, 7 in each section, in which the amount of air could be individually adjusted.

The combustion air can be preheated up to 90 and 140°C. Further possibilities of control were the supply rate of the refuse to the unit, the reciprocating speed of movement of the grate bars and the rotational speed of the clinker discharge roll at the end of the grate.

Optimum conditions for the reclamation of iron and tin from the tin cans

Laboratory experiments have shown that it is possible to separate iron and tin by oxidation under proper conditions[1]. However, experiments with gaseous HCl have shown that it is possible to separate iron and tin after incineration, even in the alloyed state. The method also gives rise to the reclamation of the separated tin[2]. The passage of tin cans through an incinerator inevitably involves oxidation losses. For the sake of iron and tin reclamation, the oxidation losses must be minimised. It is, therefore, obvious that the operating conditions of the incinerator must be adjusted such that oxidation losses are kept as low as possible. To facilitate fast detinning, the tin penetration depth must be kept small.

At above 730°C, the depth of penetration of tin as a result of diffusion increases, in principle, with the square root of time, but exponentially with temperature. The oxidation of the tin-plate too increases in principle with the square root of time and exponentially with temperature in the presence of an excess of air.

Therefore, the maximum temperatures have to be kept as low as possible with minimum exposure times. The minimum temperatures on the other hand can be raised so that complete decomposition of the garbage, adequate steam production and a satisfactory incineration capacity can be maintained.

Initial experiments with the refuse incinerator

Experiments with the refuse incinerator were performed to determine the effect of incineration on the state of the tin cans under normal and abnormal working conditions. The variety in design and composition of the tin cans in current use is very large, and in most cases it is impossible to recognize the original state after incineration. Therefore, a number of marked cans of known composition were sent with the flow of refuse through the incinerator on four successive days. After incineration, these cans were collected from the ashes and submitted to further investigation.

On the first day the working conditions were normal. On the next days, the operating conditions were successively changed, viz. (a) the distribution of primary combustion air, along the undergrate compartments; (b) the temperature of the combustion air; (c) the speed of the reciprocating movement of the grate bars; (d) the speed of the clinker discharge rolls.

During the experiments the following requirements for satisfactory operation had to be

fulfilled; (i) sufficient steam production; (ii) complete decomposition of the carbon containing portions; (iii) fast burning of the gases developed; (iv) low grate temperatures; (v) sufficient incineration capacity.

The operating conditions on the various days are given in Table 1.

Table 1. Operating conditions on the various days

	First day	Second day	Third day	Fourth day
Preheater of primary combustion air	In operation	Out of operation	Out of operation	In operation
Temperature	90 – 100°C	10°C	10°C	90 – 100°C
Grate speed	Normal (65 – 70 seconds for one reciprocating movement with a stroke of 38 cm)	Normal	Increased (55 seconds for one reciprocating movement with a stroke of 38 cm)	Increased
Distribution of primary day combustion air	Normal	In sections 2 and 3 decreased, in other sections increased	Idem as on second	Idem as on second day
Speed of the clinker rolls	Normal	Normal	Reduced	Reduced
Steam production	Normal	Normal	Normal	Normal
Decomposition of the garbage	Normal	Not sufficient	Normal	Normal

Design and composition of the cans used for the experiments

To make it possible to distinguish the marked cans from the ashes after incineration, the dimensions of the used cans were chosen to be considerably larger than those of the usual food cans, i.e. a height of 180 mm and a diameter of 180 mm.

The thickness of the electrolytic tin-plate used for the cans was 350 μm, the bottom with E-1 designation (0.4 μm tin), the body with E-2 designation (0.8 μm tin). Approximately 0.5% of the total weight of the cans was tin. Bottom and body were joined by means of a folded seam. The seam in the body was a welded lap seam; soldered seams are not used with this type of can. The cans had removable lids, which were not, however, used during the experiments in order to create the same corrosion conditions for all the cans. The cans were decorated externally, whereas the inside was lacquered.

To prevent deformation during removal from the quenching tub by the reciprocating discharger such that the cans might not be recognized, they were reinforced at the inside, although in such a way that inside corrosion could take place.

Treatment of the cans after experiments

Each can sent through the incinerator and subsequently recovered from the ashes was weighed, dried, weighed, cleaned from loose oxides and ashes and weighed again.

The separated ashes, oxides and the residues of the tin cans were all analyzed for iron and tin content.

ANALYSES

From the different series of cans sent through the incinerator on successive days the loss of iron and tin was determined.

In each can the depth of tin diffusion in the folded seam joining body and bottom was

measured by means of microprobe analyses in three different places at regular intervals along the circumference. A survey of the results of the analyses is given in Tables 2 and 3.

Table 2. Results of analyses

	First day	Second day	Third day	Fourth day
Average oxidation loss	48.8 %	42.7	33.9	46.8
S.D.	7.7	18.6	15.3	17.9
Average tin content in the non-oxidizedrest of the tin-plate after passage through the incinerator	0.40%	0.35	0.31	0.40
S.D.	0.15	0.23	0.11	0.10
Average tin penetration depth in the seams (μm)	14.1	14.0	12.2	13.9
S.D.	4.5	5.6	4.8	5.3
Number of cans send with the flow of refuse through the incinerator	15	15	15	15
Number of cans collected after incineration	13	13	14	11

Table 3. Material balances

(a) Tin balance in per cent of the original tin

	First day	Second day	Third day	Fourth day
Tin in the loose oxides and ashes, adhering to the cans after incineration	10.7	5.4	9.5	5.4
Tin in the non-oxidized part of the cans	34.7	34.5	39.2	32.2
Total	45.4	39.9	48.7	37.6
Loss of tin during passage through the incinerator	54.6	60.1	51.3	62.4
Part of the original tin, attacked by oxidation and chlorination	65.3	65.5	60.8	67.8

(b) Quantity and composition of the loose oxides and ashes, adhering to the cans after incineration (in dry condition)

Loose oxides and ashes as percentage of the total weight of the polluted iron from the incinerator	54.9	36.1	33.9	36.5
Iron content in the loose parts (%)	36.4	37.1	31.7	29.2
Tin content in the loose parts (%)	0.09	0.08	0.09	0.09
Content of ashes and bonded oxygen in loose parts (%)	63.5	62.8	69.2	70.7

DISCUSSION OF THE RESULTS

The cans chosen for the experiments have a larger size than the majority of the cans present in

the garbage. It is therefore possible that they are exposed to unrepresentative conditions. It is obvious that, because of their larger dimensions, they are more seriously deformed during mechanical ejection from the quenching pit. As a consequence a larger part of the oxidized layers could be rubbed off during ejection. Part of the cans normally present in the refuse are partly or totally closed, filled with garbage or covered with paint.

Iron balance

From the analyses, it appears that about 35 – 50% of the original weight of the cans is converted into iron oxides (Fig. 1). These oxides consist of FeO, Fe_2O_3 and Fe_3O_4. A portion of these oxides remains in the incinerator during passage. This mainly happens in the quenching pit, where the hot ashes are quenched with water and then ejected mechanically. The rest of the oxide containing about 10 – 20% of the original iron, is left behind in the wet ashes which adhere to the cans.

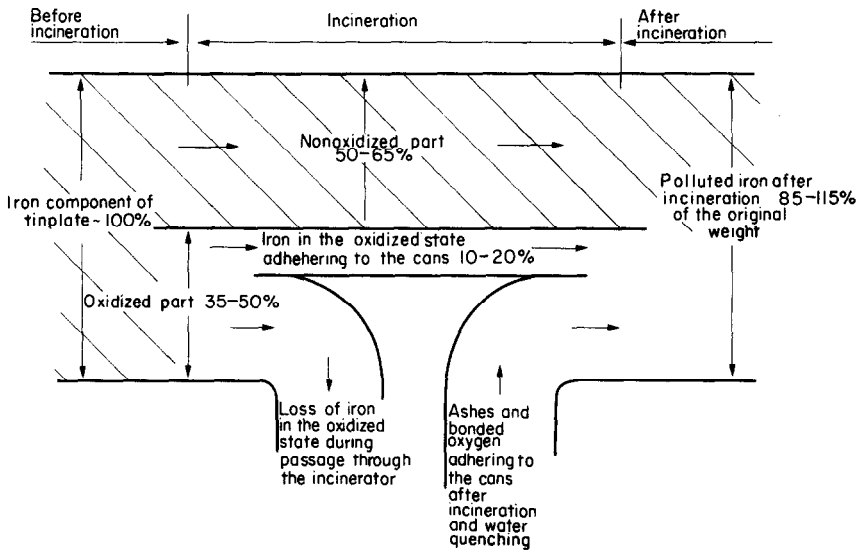

Fig. 1. Flow diagram of iron.

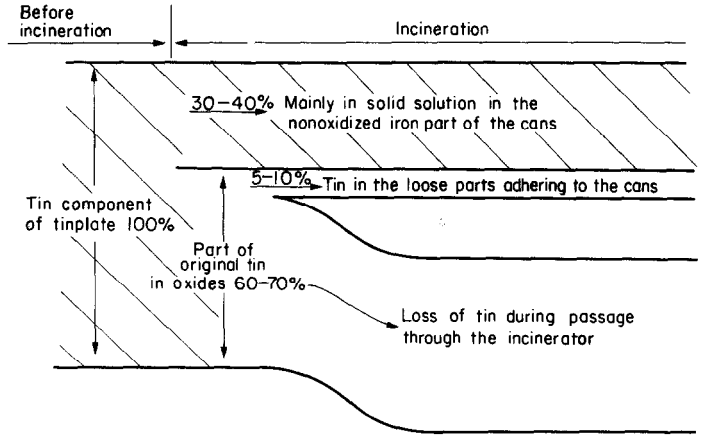

Fig. 2. Flow diagram of tin.

Tin balance

About 30 – 40% of the original tin is still present in the non-oxidized part of the cans after passage through the incinerator (Fig. 2). As a result, the corresponding tin percentage left in the non-oxidized iron amounts to approximately 0.4 and 0.3%, respectively.

From measurements made in the electron microprobe it appeared that free tin no longer existed, but that a small part of the tin was present in the intermetallic iron – tin compounds, the main part having formed a solid solution with the iron base. The rest of the original tin was present in the oxidized layers at the surface, partly as SnO_2 and partly as intermetallic iron – tin compounds. The bulk of these oxidized layers remained in the incinerator.

As a result of the presence of chlorine-containing components of the refuse, such as PVC, formation of gaseous HCl may take place during incineration. The combination of this HCl and tin can form the volatile $SnCl_2$. In the presence of water vapour, this $SnCl_2$ can be converted into the solid SnO_2, which is caught with the fly ash in the electrostatic precipitator.

From analyses of the fly ash it could be concluded that the tin present in the fly ash was equal to approximately 15 – 20% of the original tin on the cans, assuming the original average tin content to be about 0.5%. This, however, is a generalized statement. Part of the fly ash was not precipitated and the exact amount of tin on the cans, as normally present in the garbage in their original state, was not known. Further, tin from other sources will be present, such as soldered joints, tinned copper cables, tin-containing alloys, organo-tin compounds used in stabilized PVC, etc.

After ejection from the quenching pit, the oxide layers and ashes adhering to the cans contained only about 5 – 10% of the original tin. The tin content of these loose parts amounted to about 0.1% of their total weight.

From the above, it could be concluded that, probably, more than 40% of the original tin was removed from the cans during ejection from the quenching pit.

Contamination of the cans

After incineration, two kinds of contamination can be distinguished, defining the quality of the remaining tin-plate: (1) The contamination by loose oxides and ashes adhering to the cans, and (2) the contamination of the remaining non-oxidized iron parts by diffused tin.

With reference to point (1) above, wet ashes and oxide layers adhered to the cans, partly due to the wet quenching method. For the different series, these parts represented about 35 – 55% of the total weight of the contaminated cans in the dried condition. The iron content in the loose parts varies between about 30 and 37% and correspond to about 10 and 20% of the original tin-plate.

With reference to point (2) above, whereas the original tin content of the cans used for the experiments amounted to approximately 0.5%, the average tin percentage in the remaining non-oxidized cleaned tin-plate varied between 0.3 and 0.4% after passage through the incinerator. This tin was mainly present in solid solution in the iron base. The seams of the cans used for these experiments contained approximately 8% of the total amount of the original tin. After incineration, the seams and rims of most of the cans still existed. Due to the presence of tin in the seams of the cans, complete detinning by oxidation can never take place. With complete detinning of the body by means of oxidation with, say, an iron loss of 20%, the tin content as a result of the presence of tin in the seams still remains at about 0.05%. With higher losses of iron by oxidation, this tin percentage will be higher, too.

Samples taken at random from cans after incineration and analysed for Cu did not show a higher concentration after removal of the loose parts than originally present in the steel sheet, used (0.2% Cu).

Consequences of the change of the operating conditions on the condition of the tin-plate cans

Tables 2 and 3 show that the best results were obtained with the firing conditions of the third day: an oxidation loss of 34% against a 50% loss under normal working conditions; a tin content of 0.3% corresponding to approximately 40% of the original tin against approximately 0.4% representing about 35% of the original tin under normal conditions.

From Table 1 it appears that although the operating conditions on the second day were rather favourable for the condition of the tin-plate, the decomposition of the garbage does not meet the minimum requirements. Raising the speed of the grate in question does not only mean that the speed of the flow of refuse was higher, but also that a better mixture was obtained. As a result, the deviation in temperature is smaller while the deviation in the state of oxidation of the tin-plate decreases. Reduction of the speed of the clinker rolls causes a longer residence time of the garbage on the last sections of the grate, realizing a better decomposition.

The average total residence time of the garbage in the incinerator on the third and fourth day remained the same as on the first and second day.

Part of the surface of the grate is used for drying, degassing and igniting the garbage supplied. Further experiments will be carried out, using a larger part of the grate surface for the decomposition itself by accelerating the process of drying and degassing on the first sections of the grate.

AFTER-TREATMENT CF THE TIN-PLATE

The major technical problems resulting from the use of scrap with steelmaking are caused by contaminants which have a disadvantageous effect on: (a) the steelmaking process, e.g. by causing furnace damage, and (b) the mechanical properties of the steel product.

The oxides and ashes present on the tin-plate after incineration contain elements which, if present in uncontrolled amounts, can be assigned to category (a) as well as to category (b). The most important contaminants present in scrap are copper and tin. These elements are not removed during steel-making and remain in the final steel product adversely affecting the mechanical properties of the steel produced.

Dependent on the concentration of Cu and the nature of the application, e.g. for construction steel such as reinforcing bars, or for deep drawing steel such as for automobile body sheet, a tin content of 0.05 to 0.02% is permitted[3]. Cast iron has a higher tolerance for tin.

In consequence of the strong contamination by ashes as well as by the high residual tin content, it is therefore advisable to introduce methods to improve the quality so that scrap can be used in steelmaking processes as well as in blast furnaces. By-passing the blast furnace gives rise to a better use of the energy content of scrap.

After-treatment by means of gaseous HCl in the way as described in a separate publication[2] results in a remarkable lowering of the tin content of the tin-plate in which tin has gone into solid solution. Even the tin present in the seams can be removed in this way, resulting in a residual tin content of less than 0.05%. Iron losses do not exceed 5%.

The method offers the possibility of reclamation of the extracted tin constituents at the same time. Even tin from the tin oxide and compounds present in the loose oxide layers can be reclaimed. Application of this method in combination with a dry method for removal of the iron parts from the incinerator is one of the obvious combinations.

Reduction of the volume/weight ratio by shredding is advisable in order to minimise transport costs.

CONCLUSIONS

Summarizing, it may be concluded that, without modification of the incinerator, it is possible to adjust the firing conditions in such a way that it will be possible to obtain a reduction in oxidation losses of iron as well as of tin. It is expected that further work will effect a further improvement.

For the improvement of the final quality of the iron and to facilitate the reclamation of tin, a complementary treatment is necessary. The method developed transforms the nearly worthless iron product into a high-quality steel scrap.

Besides the technical research still to be carried out, it will be advisable to evaluate the economics of the upgrading methods that seem feasible. Full-scale experiments will give data from which the possibilities may be evaluated. Criteria such as environmental pollution and exhaustion of materials and energy resources have to be taken into account. Potential users of the obtained products have to be convinced of the stability in quality and quantities of supply.

Further work will be performed. State aid could accelerate the research in this field.

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